Kinetics of Phase Growth in Nb_3Sn Formation for Heat Treatment Optimization

E. Barzi and S. Mattafirri

Abstract— **The kinetics of growth and superconducting properties of Nb_3Sn are investigated as a function of the heat treatment (HT) duration and temperature for Internal Tin and Powder-in-Tube strands at 650, 700 and 750°C. For all times and temperatures, the Nb_3Sn layer thickness is measured, the critical current at 4.2 K is tested as a function of magnetic field, and the upper critical field is evaluated. Results of the layer critical current density are also shown as a function of HT duration and temperature.**

Index Terms— **Critical current density, growth kinetics, heat treatment, Nb_3Sn.**

I. Introduction

The development of high critical current density (J_c) multifilamentary Nb_3Sn wires is fundamental for many technological applications, including the design of high field accelerator magnets, whose target J_c for cost-efficiency is about 3000 A/mm^2. Although there exist extensive studies on the superconducting properties of Nb_3Sn composites, very small metallurgical information is available on the kinetics of growth of the A15 compounds. The understanding of the kinetics mechanisms of formation and growth of Nb_3Sn will allow choosing the heat treatment (HT) that gives the best superconducting properties, in addition to determining an optimimum filament size. The I_c of Nb_3Sn superconducting strands depends on numerous factors including volume of superconductor that formed, and its composition and grain size. The dependence of J_c on stoichiometry has been widely studied [1] as well as the dependence on grain size in relation to the flux-pinning force [2, 3, 4]. All these parameters are strongly dependent on the high temperature HT performed on the strand.

The kinetics of growth of Nb_3Sn was investigated for Internal Tin (IT) and Powder-in-Tube (PIT) strands at 650, 700 and 750°C by measuring the Nb_3Sn layer thickness after each HT, and the total superconductor area was calculated over the cross section of the strand. I_c measurements were performed for each HT at different magnetic fields from 4 to 15 T. The layer critical current density (J_{cl}), calculated over the Nb_3Sn area, was evaluated in order to obtain a relation between the superconducting properties and the HT parameters independently from the Nb_3Sn volume. The upper critical field (B_{c20}) was evaluated as a function of the HT parameters by fitting the I_c data versus magnetic fields using the MDB model [5]. By correlating the superconducting properties of Nb_3Sn to the HT parameters and to the amount of Nb_3Sn formed after HT, it is also possible to determine the optimum Nb filament size with respect to J_{cl} and B_{c20}.

II. Experimental Procedure

For this study were used strands with Sn in excess of stoichiometry and with large Nb filaments that provide an ample Nb_3Sn thickness range. The parameters of these IT (by Oxford Superconducting Technology, OST) and PIT (by Shape Metal Innovation, SMI) strands are listed in Table I. The IT strand is a hot extruded strand developed within the Superconductor National R&D Program. Short sample lengths were heat treated in an argon purged furnace at 650, 700 and 750°C for the various durations shown in Table II. The low temperature HT for Cu-Sn diffusion in the IT strand was chosen out of [6]. The samples, inserted and extracted from the furnace at room temperature, are heated up to the set point value with a ramp rate of 150°C/h.

TABLE I
STRAND PARAMETERS

Parameter	IT Strand	PIT Strand
Strand diameter [mm]	1.000± 0.001	1.005 ± 0.001
Filament size [μm]	35	50
Cu stabilizer fr. %	32.0	45.3 ± .03
Sn wt. %	20.0	not available
Nb wt. %	36.6	not available
Number of filaments	310	192
RRR	50-100	100-200

TABLE II
HEAT TREATMENTS

		IT	PIT
Pre-HT	T [°C]	400	
	Duration [h]	80	-
	Ramp rate [°C/h]	150	
HT	T [°C]	750	750
	Duration [h]	2, 5, 10, 20, 40	2, 5, 10, 20, 40
	T [°C]	700	700
	Duration [h]	5, 10, 20, 40, 80	5, 10, 20, 40, 80
	T [°C]	650	650
	Duration [h]	50, 100, 200, 400	50, 100, 200, 400
	Ramp rate [°C/h]	150	150

Manuscript received August 5, 2002. This work was supported by the Department of Energy in part under contract Number DE-AC03-76SF00098.
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The temperature, monitored with a thermocouple, follows approximately the same ramp rate during the cool down of the chamber.

The Nb_3Sn thickness is measured after each HT with a high resolution optical microscope. The average value of the thickness for each HT is computed by measuring the area of the Nb_3Sn outer circle and of the circular unreacted Nb over four Nb filaments. The standard deviation on the average thickness is taken as a measure of the thickness uncertainty, which for all HTs was within 0.7% and 4.7% for the PIT strand and within 2% and 15.9% for the IT strand [10]. The systematic effect on the thickness due to the transients of the HT is evaluated by measuring the thickness formed after the ramp to maximum temperature and assuming a $y^n = kt$ dependence of the thickness on the HT duration [7]. The systematic effect, while negligible for the IT strand, is within + 0.7% and + 10.4% for the PIT strand since a substantial thickness of Nb_3Sn already forms below 650°C.

The samples used for I_c measurements were wound on grooved cylindrical Ti-alloy barrels as in [8]. The estimated uncertainty of the I_c measurements is a function of the transport current and of the magnetic field [9]. At 4.2 K and 12 T it is about ±5% for the IT strand and less than ±1% for the PIT strand. The upper critical field B_{c20} is evaluated for each HT by fitting the I_c data versus the magnetic field using the MDB model [5] and the least square method. The uncertainty on B_{c20} was evaluated by measuring the latter sensitivity to I_c fluctuations [9]. The systematic effects due to the tensile strain and to the self-field of the sample were within +1.1 and 0 T.

III. Nb_3Sn Kinetics of Growth

The layer growth of Nb_3Sn in the PIT and IT strands is shown in Fig. 1 as a function of temperature and HT duration. It can be seen that the layer growth is strongly dependent on temperature and shows a large gain above 700°C. This could be due to the melting of most Cu-Sn phases above this temperature. The thickness formed in the PIT strand is larger than that formed in the IT strand. In addition, in the former case the HT ramps introduce a measurable systematic effect [7]. During superconductor growth, the Cu-Sn matrix in the IT strand and the Nb_2Sn matrix in the PIT strand undergo a substantial Sn depletion. For instance, after 40 h at 750°C, the Sn composition in the IT strand varies from the initial 20 wt.% to 4.3 wt.%. Under these conditions the hypotheses for the parabolic growth law [10] are not verified and the Nb_3Sn growth rate depends on Sn composition as well as on the strand technology. Fig. 2 shows the cross sections of both strands after 40 h at 750°C. In both cases, voids are present at the interface between the Nb_3Sn and either the bronze matrix for the IT strand or the Nb_2Sn matrix for the PIT strand.

IV. Superconducting Properties

The I_c at 12 T and 4.2 K is shown in Fig. 3 for the PIT (top) and IT strands (bottom) as a function of HT duration at 650, 700 and 750°C. Initially the I_c increases rapidly with time, then in most cases appear to reach a plateau. The maximum I_c values are obtained after 80 h at 700°C, after 400 h at 650°C

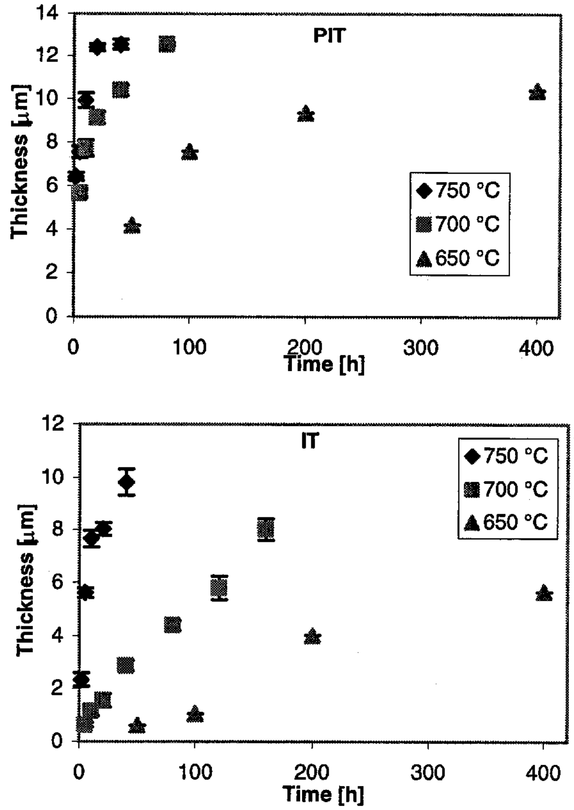

Fig. 1. Nb_3Sn layer growth as a function of HT time and temperature for the PIT (top) and IT (bottom) strands.

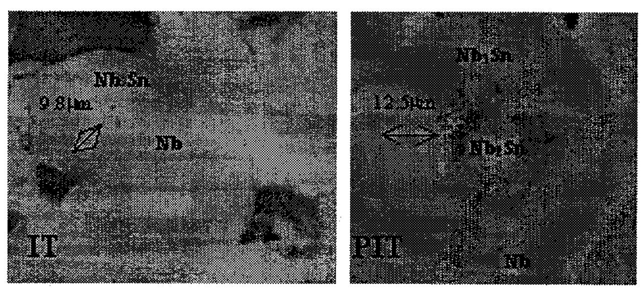

Fig. 2. Nb_3Sn growth in IT and PIT strands after 40 h at 750°C.

and after 62h at 675°C for the PIT strand, and after either 80 h at 700°C or 40 h at 750°C for the IT strand. It was observed that after 5 h at 700°C the IT strand is not superconducting at any magnetic field even if a 0.6 µm layer of Nb_3Sn intermetallic compound is formed. At the same temperature after 10 h the I_c was measured to be zero above 14 T. This suggested that this early compound has a lower B_{c20}. Fig. 4 shows J_{cl} at 12 T and 4.2 K and B_{c20} as a function of HT times at 750, 700, and 650°C for the PIT strand. The J_{cl} peaks after 10 h at 750°C and after 40 h at 700°C. A high J_{cl} value is obtained, similarly to the one obtained for the latter HT, also after 400 h at 650°C. The B_{c20} behavior shown in Figure suggests an initial off stoichiometry composition of the Nb_3Sn compound that approach to an ordered stoichiometric state only after adequately increasing the HT time.

Fig. 5 shows J_{cl} at 12 T and 4.2 K as a function of HT times at 750, 700 and 650°C for the IT strand.

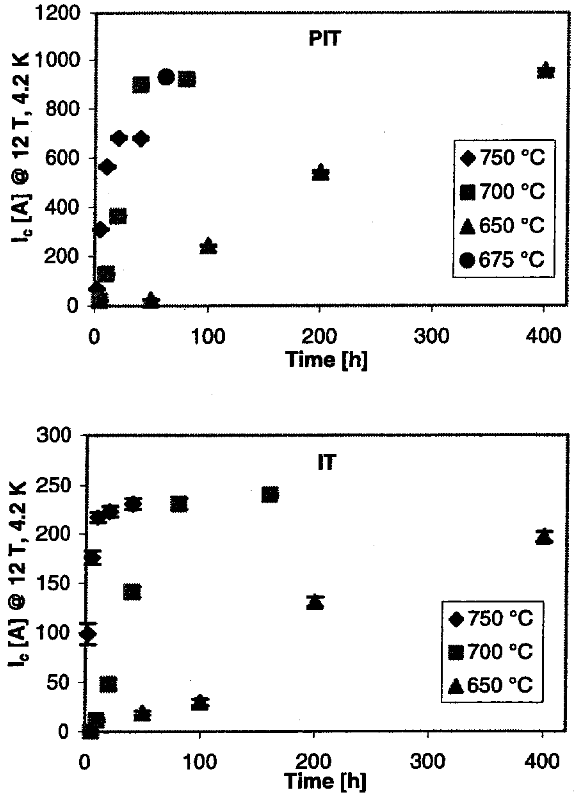

Fig. 3. I_c at 12 T and 4.2 K as a function of HT time and temperature for the PIT (top) and IT (bottom) strands.

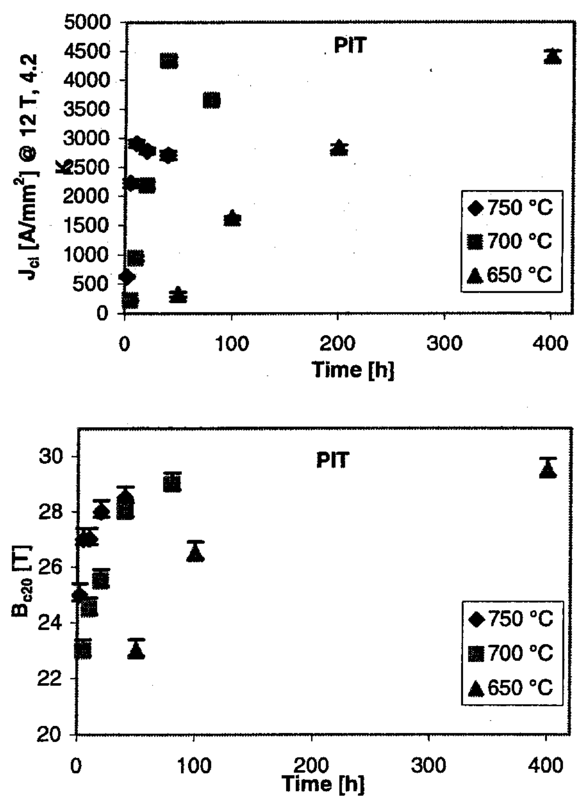

Fig. 4. J_{cl} at 12 T and 4.2 K (top) and B_{c20} (bottom) as a function of HT time and temperature for the PIT strand.

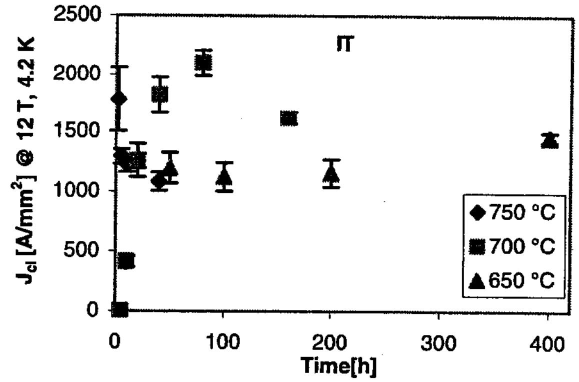

Fig. 5. J_{cl} at 12 T and 4.2 K as a function of HT time and temperature for the IT strand.

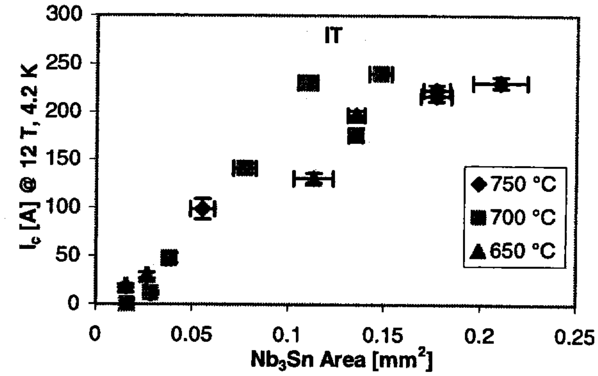

Fig. 6. I_c at 12 T versus Nb_3Sn area for the IT strand at all HT times and temperatures.

In this case, 750°C appears to be the temperature for fastest stoichiometry, as confirmed by the B_{c20} plot (not shown), but its rapid decrease with time indicates fast grain growth. The maximum J_{cl} is obtained at 80 h at 700°C, which is also the HT that provides the maximum I_c. Actually, the I_c vs. Nb_3Sn area plot of Fig. 6 shows the superiority of 700°C with respect to the other temperatures, in that the I_c to superconductor area ratio is always the largest. This is not true for the PIT strand, for which both 650 and 700°C give good performance.

V. Discussion

For both IT and PIT, a fraction of the Nb filament is still unreacted with the HT cycle that gives the maximum J_{cl}. For the IT strand, a higher I_c could be obtained (for the same strand diameter) by increasing the number and decreasing the diameter of the Nb filaments in order to complete the Nb transformation in Nb_3Sn with the highest J_{cl}. The filament size that would allow obtaining the largest I_c should be about 10 μm. For the PIT strand, the best I_c could be obtained by choosing the appropriate tube thickness. A RRR analysis showed that an unreacted thickness of about 2 μm is sufficient to produce RRRs larger than 100. Since 40 h at 700°C, which formed about 10.5 μm of superconductor, produced the best J_{cl}, a tube thickness of about 13 μm would be optimal. However, this might not be adequate with respect to technological issues like Rutherford cabling degradation. The above filament size estimates are affected by the uncertainty that the parameters measured for a particular geometry and composition are not necessarily reproducible for other strand designs.

The Nb_3Sn growth versus HT parameters, due to the Sn depletion, depends on the composition besides on the strand technology. References values for the growth rate (k) were however evaluated by fitting the thickness data (y) versus HT duration (t) using a $y^n = kt$ dependence [11] and the least square method.

TABLE III
Nb_3Sn GROWTH RATE. REFERENCE VALUES

T [°C]	PIT k [cm^n/s]	PIT n	IT k [cm^n/s]	IT n
750	6.9 10^{-24}	3.7	6.3 10^{-17}	2.3
700	1.2 10^{-23}	3.6	1.5 10^{-14}	1.5
650	5.0 10^{-18}	2.3	2.0 10^{-11}	0.9

The deviation from the parabolic growth law, can be attributed to the depletion of the Sn inside the matrix for $n > 2$, or to crack in the layer for $n < 2$ [12], that accelerate the diffusion process. However some deviations in this case can also be due to the non planar geometry interface between Nb and the matrix and to the variation of the Sn concentration gradient along the Nb_3Sn interlayer during the growth. The non constant concentration gradient is due to the large range of composition of the Nb_3Sn intermatallic compound (18%a-25%a Sn). The composition of the Nb_3Sn layer seems also to vary with the HT temperature and time, as it is shown by the trend of the B_{c20}. This could also explain the different growth law exponent found for the three temperatures.
The evaluation of the J_{cl} and of the B_{c20} gives the possibility to obtain an observed relation between the effects of the grain growth and of the composition changes as a function of the HT parameters on the I_c. The gain on I_c with Nb_3Sn volume is vanished by the decreasing of pinning centers with increasing the HT duration especially at high temperature.

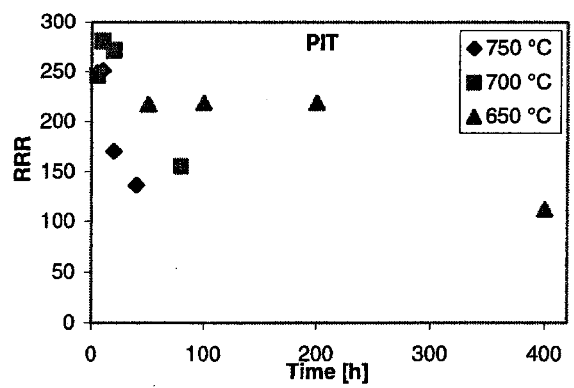

Fig. 7. RRR for PIT strand as a function of HT duration at 750, 700 and 650°C.

It is worthwhile to mention also that the RRR measured for both strands in function of the HT parameters and shown in Fig. for the PIT strand, even if decreased for all the temperatures with increasing the HT time, resulted above 100 for all the HTs. For the IT instead, the RRR resulted above 100 only for very short time reaction (less than 5 h at 750 °C and less than 40 h at 700 °C) [7].

The n value, while quite constant (around an average value of 11) for the IT strand with HT parameters, was observed to reach a peak value (in the order of 65) for all the HT temperatures for the PIT [7].

IV. CONCLUSIONS

The growth of the Nb_3Sn intermetallic compound has been related to the HT duration at 750, 700 and 650°C for two IT and PIT strand designs. For both the strands technology PIT and IT with large filament design, the HTs that give the highest I_c have been evaluated.

The information on the superconducting properties of the wires is obtained independently from the volume of the Nb_3Sn thanks to the J_{cl} and B_{c20} evaluation. The HTs that lead to the highest J_{cl} are evaluated for both the two strands technology. Thanks to the correlation between the Nb_3Sn volume and the HT parameters it has been possible to obtain an estimate of the Nb filament size for the IT and of the Nb tube thickness for the PIT that should lead to an improvement of I_c by the complete transformation of Nb into Nb_3Sn with the highest J_{cl}.

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